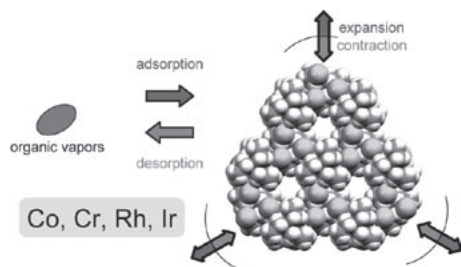


and organic vapors accompanying the expansion of channel in its crystal structure.[1] To investigate the possibility of single crystal of tris-ethylenediamine metal complexes as ionic single-crystal hosts for vapor adsorption, a series of adsorbency of single crystals of $[M^{III}(en)_3]Cl_3$ ($M = Co, Cr, Rh, Ir$) were studied. All complexes have channels in their crystal structures, which dynamically and reversibly change their size with vapor adsorption, and show similar vapor adsorbency like the adsorption behavior of $[Co(en)_3]Cl_3$. [2]

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[2] S. Takamizawa, M. Kohbara, T. Akatsuka, R. Miyake, submitted



Keywords: gas-solid inclusion reaction, solid-state structural changes, ionic crystals

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Synthesis and properties of dioxalatocuprates (II) and ruthenium (III) aminocomplexes salts

Evgeny Yu. Filatov^{1,2}, Svetlana A. Martynova¹, Sergey V. Korenev^{1,2}, Yuriy V. Shubin^{1,2}

¹Nikolaev institute of inorganic chemistry, Siberian Branch of Academia of Science, Lavrentev ave. 3, Novosibirsk, Novosibirsk region, 630090, Russia, ²Novosibirsk State University, Pirogova str. 2, Novosibirsk, Novosibirsk region, 630090, Russia, E-mail: decan@che.nsk.su

Double complex salts (DCS) are of great interest as precursors of bimetallic solid solutions and intermetallics. Solid solutions based on platinum group metals have high catalytic activity. Thermolysis such single-source molecular precursors under low temperature (400 °C) allows to prepare bimetallic powders with definite ratio of components and particles size about 5-10 nm. This work related to synthesis of complexes contained simultaneously ruthenium and copper and study of their metallic thermolysis products. In the field of this work the following DCS were synthesized: $[Ru(NH_3)_5Cl][Cu(C_2O_4)_2] \cdot H_2O$ (I), $[RuNO(NH_3)_4OH][Cu(C_2O_4)_2] \cdot 1.5H_2O$ (II). Obtained DCS were characterized by IR-spectroscopy, element analysis, XRD and X-ray single crystal analysis. This is crystallographic data: (I) $a = 7.6277(5)$, $b = 13.1052(8)$, $c = 14.9640(7)$ Å, $\beta = 97.852(2)$, $V = 1481.81(15)$ Å³, $P2_1/n$, $Z = 4$, $D_x = 2.148$ g/cm³; (II) $a = 7.1121(2)$, $b = 10.3941(3)$, $c = 10.6288(3)$ Å, $\alpha = 97.0340(10)$, $\beta = 107.6150(10)$, $\gamma = 92.8600(10)$, $V = 740.10(4)$ Å³, $P-1$, $Z = 1$, $D_x = 2.276$ g/cm³. Structures are build of discrete $[Ru(NH_3)_5Cl]^{2+}$, $[RuNO(NH_3)_4OH]^{2+}$, $[RuNO(NH_3)_5]^{2+}$ cations and $[Cu(C_2O_4)_2]^{2-}$ anions. Thermolysis of obtained salts under inert and reduction atmosphere was studied. The XRD investigation of thermolysis products was carried out. Decomposition of salts under helium atmosphere begin at 140 - 150°C, occur in 2 stages and finish at 520°C (I), at 300°C (II). Thermolysis products are Ru, RuO₂, CuCl, Cu₂O. Decomposition of complexes under hydrogen atmosphere also studied. Product is Ru_{0.8}Cu_{0.2}. This work was supported by the RFBR grants 07-03-01038-a, 08-03-00603-a.

Keywords: double complex salt, ruthenium, copper

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Synthesis and crystallographic study in the PbO-Bi₂O₃-V₂O₅ System: Pb_{3-x}Bi_{2/3x}V₂O₈

Prangya Parimita Sahoo¹, Etienne Gaudin², Jacques Darriet³, Tayur N Guru Row⁴

¹Indian Institute of Science, Solid State and Structural Chemistry Unit, C. V. Raman Avenue, Bangalore, Karnataka, 560012, India, ²Institut de Chimie de la matiere condensee de Bordeaux, 33608 Pessac Cedex, France., ³Institut de Chimie de la matiere condensee de Bordeaux, 33608 Pessac Cedex, France., ⁴Indian Institute of Science, Solid State and Structural Chemistry Unit, Bangalore, Karnataka, 560012, India, E-mail: prangya@sscu.iisc.ernet.in

PbO-Bi₂O₃-V₂O₅ System is of current interest owing to its use to generate novel ion conducting materials [1]. Pb₃V₂O₈ displays two structural phase transitions at 373 and 273 K [2]. The first order phase transitions have been studied both by neutron and X-ray powder diffraction [3]. The high temperature γ phase of Pb₃V₂O₈ adopts the palmerite structure [4, 5]. In this context, polycrystalline samples in the series Pb_{3-x}Bi_{2/3x}V₂O₈ ($x = 0.2$ to 1.5) have been synthesized by solid-state route. The compositions $x = 0.2$ to 0.7 form a solid solution with a structure similar to γ form of Pb₃V₂O₈, as confirmed by powder diffraction studies while Pb₃BiV₃O₁₂ ($x = 1.0$) was isolated from a mixture of two phases. Single crystals of both phases representing two new vanadates were grown by melt-cool technique. Pb_{2.5}Bi_{1/3}V₂O₈ ($x = 0.5$) and Pb₃BiV₃O₁₂ ($x = 1.0$), have been analysed by single-crystal X-ray diffraction. Pb_{2.5}Bi_{1/3}V₂O₈ crystallizes in a trigonal system, space group $R-3m$, with $a = 5.755(6)$ Å, $c = 20.317(4)$ Å, $V = 582.74(1)$ Å³ and $Z = 3$ whereas Pb₃BiV₃O₁₂ is cubic (eulytite), space group $I-43d$, with $a = 10.749(2)$ Å, $V = 1241.9(1)$ Å³ and $Z = 4$. It is of interest to note that this study for the first time describes the structural motifs formed by a eulytite vanadate.

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Keywords: synthesis, solid solution, powder and single crystal diffraction

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Photoinduced surface relief grating formation using single crystals of azobenzene derivatives

Hideyuki Nakano

Osaka University, Department of Applied Chemistry, Faculty of Engineering, Yamadaoka, Suita, Osaka, 565-0871, Japan, E-mail: nakano@chem.eng.osaka-u.ac.jp

Surface relief grating (SRG) formation by irradiation of amorphous films of azobenzene-containing polymers with two coherent laser beams has recently received a great deal of attention in view of both academic interest and potential technological applications. We have been performing studies of the photoinduced SRG formation using azobenzene-based photochromic amorphous molecular materials. Photoinduced SRG formation is believed to take place by mass transport induced by *trans*-*cis* and *cis*-*trans* isomerizations of azobenzene chromophore. Several models for the mechanism of the SRG formation have been proposed; however, the details have not been clear yet. In contrast to amorphous materials, it is of interest to

examine whether fabrication of SRG on the organic “single crystal” is possible or not by irradiation with two coherent laser beams. If possible, the study of photoinduced SRG formation using single crystals may provide information about not only the mechanism of the SRG formation but also the molecular motion near the surface of the organic crystal. In the present study, photoinduced SRG formation on an organic single crystal has been demonstrated by using 4-(dimethylamino)azobenzene. It was found that the SRG formation was greatly depending upon both the orientation of the crystal and the polarization of the writing beams. The dependence of the polarization of the writing beams on the SRG formation using the single crystal was found to be quite different from that reported for amorphous polymers and photochromic amorphous molecular materials.

Keywords: photochromism, surface morphology, materials science

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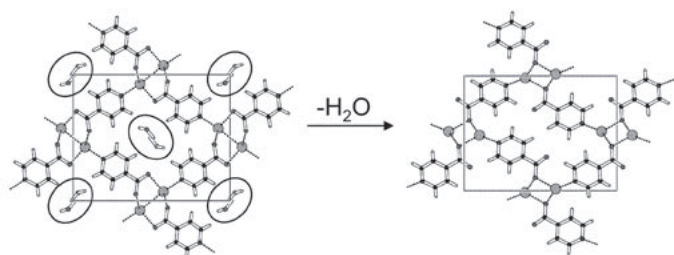
From crystal to crystal: Dehydration of (4-carboxylato)-silver(I) monohydrate

Ulli Englert, Irmgard Kalf, Patrick Mathieu

RWTH Aachen University, Institute of Inorganic Chemistry, Landoltweg 1, Aachen, NRW, 52074, Germany, E-mail : ullrich.englert@ac.rwth-aachen.de

(4-carboxylato)silver(I) monohydrate was obtained via reaction of isonicotinic acid and silver carbonate. The resulting three-dimensional coordination polymer was described recently. [1] The left part of the figure shows a projection of the unit cell in which the water-containing voids have been highlighted. The solvent molecules do not strongly interact with the framework. Under vacuum the topotactic dehydration of this monohydrate to its unsolvated form (Figure, right) occurs. The reaction proceeds as single-crystal-to-single-crystal transformation and is irreversible. During the topotactic desolvation, the 3D framework transforms into a two-dimensional layer structure.

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Keywords: topochemistry, coordination polymer, single-crystal-to-single-crystal transformation

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Synthesis and characterization of $TAgM_3X_6$ (T = Mn, Fe; M = Sb, Bi; X = Se)

Chi-Shen Lee, Nei-Lun Cheng

National Chiao Tung University, Applied Chemistry, 1001 University Road, Hsinchu, Taiwan, 30010, Taiwan, E-mail : chishen@mail.nctu.edu.

tw

Three new quaternary selenides $TAgM_3X_6$ (T = Mn, Fe; M = Sb, Bi; X = Se) has been prepared by heating stoichiometric amounts of the constituent metals and selenium in evacuated silica tubes at 1023K. The crystal structures were determined by single-crystal X-ray diffraction and the compound crystallizes in $Ag_3Bi_7S_{12}$ structure type with monoclinic space group $C2/m$ (No. 12, Z = 4). This structure features two NaCl (311)-type slabs, which stack along *c*-axis. The transition metals Mn and Fe are essential element to synthesize these compounds. Theoretical studies performed on $MnAgBi_3Se_6$ show that the material is a semiconductor, which has been confirmed by the electric conductivity measurements. Magnetic susceptibility measurements show that the $MnAgBi_3Se_6$ materials exhibit temperature dependent paramagnetism and obey the Curie-Weiss law with high-spin state of Mn^{2+} , whereas $FeAgBi_3Se_6$ does not. The optical band gaps are ~ 0.75 eV that are estimated by diffuse reflectance measurements.

Keywords: solid-state chemistry, solid-state compounds, selenides

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Availability of solid-state polymerization of amino acid NCAs as compared with solution reactions

Hitoshi Kanazawa, Aya Inada, Arai Takayuki

Fukushima University, Faculty of Symbiotic Systems Science, Kanayagawa 1, Fukushima-shi, Fukushima Prefecture, 960-1296, Japan, E-mail : kana@sss.fukushima-u.ac.jp

In general, *N*-carboxy amino acid anhydrides (amino acid NCAs) have been polymerized in solutions to obtain high-molecular-weight polypeptides. As the solution polymerization of γ -benzyl-L-glutamate NCA (BLG NCA) has been extensively investigated, the reaction in dioxane, dichloromethane, etc. was compared with the solid-state polymerization. The solid-state polymerization was carried out by putting the NCA crystals into hexane which cannot dissolve the NCA and the polymer. Butyl amine was added as initiator. We found that the solid-state reaction was more reactive than the solution reaction, avoiding a moisture contamination (see Fig.1). The reactivity of NCA was affected by the purity of the NCAs. The polypeptides with monodisperse high-molecular-weight, which had not been prepared so far were obtained. Crystal structures of BLG, L-leucine and L-phenylalanine NCAs were found to be preferable for the polymerization in the solid state (see Fig.2). Polypeptides of alanine, valine, leucine, etc. which are not soluble in usual solvents can be prepared by the solid-state polymerization of the NCA. It is necessary to correct the misunderstanding concerning the reactivity of the NCAs.

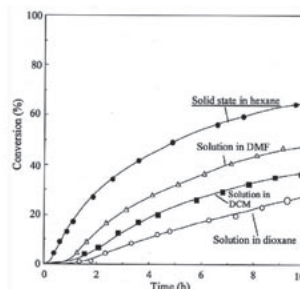


Fig.1 Time conversion curves of the polymerization of BLG NCA in the solid state in hexane and solutions at 30° C; M/I=200 and Cl content of NCA=0.0512 wt%.

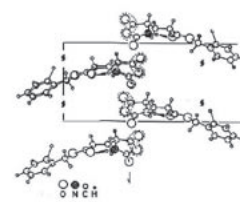


Fig.2 BLG NCA crystal (P212121)